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Recent Developments in Cement Kilns.

IN the following we give particulars of two long dry-process horizontal kilns and a gas-fired kiln recently installed in American cement works, and a description of a new type of vertical kiln developed on the Continent for the production of lime and cement.

Performance of Dry-Process Kilns 314 ft. Long.

Some information is given in "Rock Products" for June, 1947, on the performance after six months' service of two 9 ft. by 314 ft. dry-process kilns at the works of the Lawrence Portland Cement Co. at Northampton, Pennsylvania. Each kiln has an output of 250 to 265 tons of clinker a day with an average coal consumption of 390 lb. of 13,500 B.Th.U. coal per ton of clinker. These kilns are the longest operating on the dry process. It is claimed that low fuel consumption is due to the length of the kiln, and that soundness and uniformity of cement are also increased; further, there are no heat exchangers or preheating devices to add to the power requirements. Figs. 1 and 2 show the arrangement of the firing equipment and details of the feed end of these kilns.

The kilns are all-welded, and are supported on five sets of rollers and have a slope of $\frac{7}{16}$ in. as a precaution against surging when turning at a normal speed of 75 r.p.h. The drive is a 50–60 h.p. d.c. electric motor, with a speed range of 300 to 1,200 r.p.m. through a spur-gear reducer synchronised with the feed material screw drive. The cooler consists of ten 3 ft. 5 in. cylinders 17 ft. 3 in. in length, lined with heat-resistant cast steel and refractory liners because, in this installation with its high fuel efficiency, there must be some sacrifice in cooling efficiency due to the low volume of air permissible. With the exception of 17 ft. in the cooling zone and the cooler discharge, the kilns are lined with 6-in. refractory blocks for their entire lengths, the lining consisting of 70 per cent. alumina brick for 70 ft.

in the burning zone followed by 50 per cent. alumina brick and with 40 per cent. alumina brick at the feed end. In addition, each kiln has 2½ in. of special insulation between the shell and refractory bricks for 196 ft. 9 in. of its length to a point 25 ft. above the calcining zone. The refractory bricks are laid to tie to longitudinal key blocks, comprising a single row of blocks at the four quadrants to

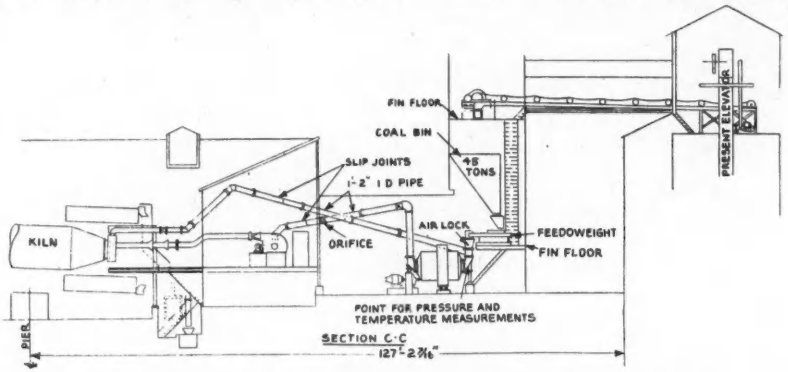

Fig. 1.—Arrangement of Firing Equipment for Kiln 314 ft. long.

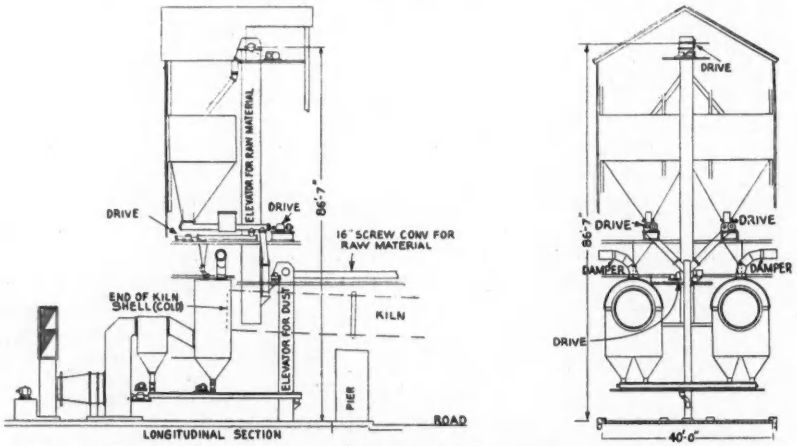

Fig. 2.—Longitudinal section (left) and End Elevation (right) of Feed End of Kiln 314 ft. long.

keep the insulation from shifting. No signs of insulation failure or breakdown were detected after four months of operation.

The kilns are fired from air-swept unit ball mills which dry the coal as it is ground and inject primary air plus pulverised coal through the kiln burner pipe as a continuous operation. The mills are in a separate building adjoining the kiln operator's floor. Ball mills are used because it was anticipated that relatively

uniform results would be attainable with wide variations in the moisture content and the size of the coal, tempered air from the kiln hood being introduced into the mills at a temperature as high as 600 deg. F. The mill has two compartments. It has no trunnions and the drive is enclosed in a single casing. The mill is supported near the centre on a combined slide-shoe ring and herringbone gear, the slide-shoe ring resting on two self-aligning slide shoes all enclosed in the single casing. The gear and slide-shoe ring are dip lubricated. At the outlet end, the mill is provided with a standard pillow-block guide bearing. A herringbone gear drive with the high ratio of reduction attainable by its use will permit the use of relatively small high-speed electric motors. A 75-h.p. slip-ring motor is used to drive a mill carrying 13,290 lb. of forged steel balls, which revolves at 24 r.p.m. and discharges a product with 80 per cent. passing a 200-mesh sieve.

Coal is fed to each mill by a 45-ton overhead bin through a weigher. An air lock is provided in the feed spout just below the feeder. Primary air is taken from the kiln hood in the ordinary way, tempered with cold air and introduced just below the air lock into the feed end. The primary air and coal are drawn through the mill by a fan driven by a 25-h.p. electric motor and blown into the kiln through an annular air-cooled pipe. Pressure and temperature measurements are made at the inlet to the coal mill and adjustments are made by a damper at the primary air fan and a butterfly valve at the coal feed pipe.

The coal mill is regulated either by an automatic feed controller or manually, according to the extent of variations in size of coal feed and moisture content. Automatic control is effected by a vibratory unit consisting of a riding contact on a track around the diameter of the mill and an amplifying box which picks up the mill vibrations and transfers through direct current electrical impulse to a controller on the kiln control board. Variations in vibrations induced under overload or underload inside the mill are reflected, when operated under automatic control, in the coal feeder drive. Primary air leaving the coal mill is not permitted to exceed 170 deg. F. The kiln is fired with only 25 to 30 per cent. of primary air, the only air entering the kiln unpreheated being the tempering air to the coal mills and that introduced through the annular opening around the burner pipe.

The method of feeding raw material into the kilns has resulted in a continuously uniform rate of feed which, in combination with a constant speed of rotation, has contributed to better uniformity of product and the absence of surging. Raw material is conveyed from the raw grinding mills by a 16-in. screw conveyor to the back end of the two kilns where a single enclosed bucket elevator fills separate hoppered-bottom feed bins over each kiln. The fineness of the feed is 88 per cent. passing a 200-mesh sieve ground in open circuit through tube mills, and its temperature is in the neighbourhood of 200 deg. F.

An ordinary adjustable horizontal slide gate is used to release the raw material to the feeder, which consists of two parallel and horizontal 12-in. screw conveyors, one superimposed over the other. They are about 25 ft. long and are housed in standard steel pipes with a clearance of only 1/32 in. between the flight and the casing and each flight has a pitch of 8 in. The upper flight, driven at constant

speed by a 10-h.p. motor through a herringbone gear reducer, turns at 37 r.p.m. compared with an average of 30 r.p.m. for the lower flight which receives its feed from the far end of the upper flight and discharges into the kiln feed spout. The upper and lower flights carry 26 tons and 20 tons of dry material per hour respectively, so that the flight which actually feeds the kiln will be always full and under a constant head of material. A surge-box on the upper conveyor flight is a precaution against packing, and an overflow pipe to the bucket elevator collects any excess circulating material that is not transferred to the feeder flight. The drive on the lower, or feed, flight is variable and synchronised with the kiln drive. Weighing of a sample of about 150 lb., drawn over a period of exactly ten seconds, has regularly shown the device to be accurate within 1 lb.

Clinker discharged from the cooler at 400 to 450 deg. F. is further reduced in temperature to 185 deg. F. through a 7-ft. by 80-ft. rotary cooler.

The kilns were supplied by Messrs. F. L. Smidth & Co.

A Gas-Fired Kiln at an American Cement Works.

A third kiln was recently installed at the works of the Calaveras Cement Co., San Andreas, California, which increases the annual capacity of this works to 2¼ million barrels. The kiln, which is described in "Concrete," August 1946, had been in use elsewhere for a while.

It is an Allis-Chalmer's kiln, 11 ft. 3 in. in diameter and 360 ft. long, and is of welded construction throughout. Its daily capacity is 3,500 barrels. The kiln is supported on five concrete piers, and turns on trunnions running in water-cooled bronze bearings. The slope is $\frac{7}{16}$ in. per foot. It is driven by a 150-h.p. variable-speed induction motor, which drives a generator connected to the motor shaft. The generator is electrically connected with the Ferris wheel and dust-return motors, so that the rate of slurry fed to the kiln, and of dust returned, is exactly proportional to the speed of rotation of the kiln, thus ensuring a uniform load in the kiln if it is necessary to alter the speed.

The method of returning dust to the kiln is believed to be novel. From the dust-screws the dust is pumped to a bin above the feed floor. From this bin the dust is withdrawn by a screw synchronised with the kiln and thence discharged into a pug-mill where it joins the slurry feed from the Ferris wheel. The slurry and dust are beaten together just before the mixture is fed to the kiln. This is found to be a very satisfactory method of returning the dust. Its advantages lie in the fact that the mixing is adequate to prevent separation in the kiln, and the dust, which has hydraulic properties, is kept out of the circulating slurry system. The dust and slurry can be proportioned to give a correct mixture to the kiln, and the uniform rate of feeding prevents the dust, which is much higher in lime than the slurry, from disturbing the proportions of the feed, and thus prevents interference with uniform burning.

The kiln is equipped with chains in order to increase the heat transfer in the drying zone. The exit gases are exhausted by a 11-ft. steel-plate double-inlet fan having a capacity of 180,000 cu. ft. per minute at 4 in. and 600 deg. F.

The clinker is discharged into a 6-ft. by 33-ft. inclined-grate cooler with automatic bed-speed control, which is operated through a thermocouple by radiant heat from the clinker bed, thus maintaining the thickness and temperature of the clinker bed approximately constant, and with uniform resistance to the flow of cooling air through it. A uniform temperature for the secondary air for combustion is thus assured ; this eliminates a variable that is troublesome in many burning operations.

The usual fuel is natural gas controlled by a recording gas controller. The burner is equipped to mix up to 45 per cent. primary air with the gas. The amount of primary air is regulated automatically. When set for a definite proportion of primary air and gas, the same proportion is maintained with any gas setting. If it is necessary to alter the proportion of gas the proportion of primary air follows automatically, so that although the amount of heat liberated in the burning zone is changed the character of the flame is not.

The louvres at the exhaust fan are operated by an automatic control, which maintains a constant hood-draught. This can be changed to manual control if desired. A duplex gauge indicates the draught at both the hood and the dust-chamber, and these draughts are at the same time recorded on two other meters so that the comparative draughts at any time are on record. The hood draught controls the amount of secondary air, and therefore the type of combustion, and a comparison of the hood draught and the dust-chamber draught is a measure of the internal condition of the kiln. Under normal operation the hood draught is zero, or minus one or two hundredths of an inch. With the kiln clear, a dust-chamber draught of a little over an inch will maintain this. Any increase in the dust-chamber draught much over an inch indicates rings or other obstructions in the kiln. Recording pyrometers on the burning floor give the burning-zone, exit-gas, and fan temperatures.

A New Type of Vertical Kiln.

In a recent number of "Revue des Materiaux de Construction," M. Joseph Deforge describes a new vertical kiln for the production of lime and cement. One of the advantages claimed for this kiln is its simplicity and the robust character of the mechanical parts. The general arrangement is shown in the accompanying diagram (Fig. 3). The bunkers A and B contain respectively the raw material and fuel. These materials are weighed automatically at C and are discharged on to the conveyors D. The materials proceed down a chute to the boot of the elevator E, which raises the materials and discharges them into the mixer F, from which they pass to a briquetting machine G. The briquettes are distributed uniformly in the kiln K, through the apparatus at H. The discharge is made through the grilles L to the hoppers M. The grilles are operated by the mechanism at N. The fan P forces air into the cavity in the walls and into the bottom of the kiln.

For the manufacture of artificial cement, the powdered raw material and the pulverised or granulated coal, after weighing, are mixed wetted, and made into small cylindrical briquettes, which are said to be preferable to the blocks

of large dimensions commonly used. The preliminary heating is effected within 6 ft. below the orifice through which the kiln is charged. The cylindrical briquettes, because of their small volume, are very rapidly affected by the heat which dries and hardens them, thus preventing their disintegration before they reach the burning zone. This zone is cooled by cold air circulating within the double wall of the kiln (that is behind the refractory lining), and so fusion of the refractory

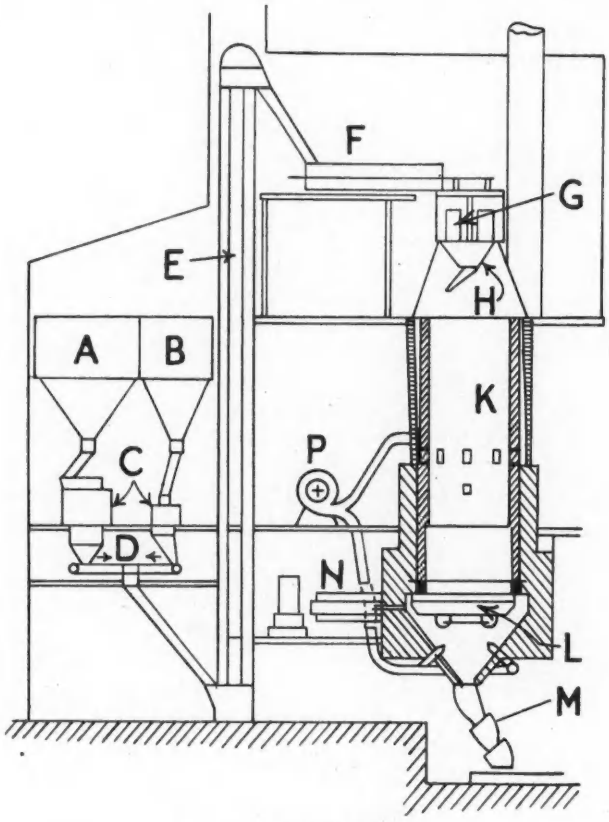

Fig. 3.—A Vertical Kiln.

bricks is prevented. Because of this, the lining has a longer life than if it were not subject to cooling.

After the air has acted as a cooling medium, and thereby become heated, the air enters the kiln at the level of the burning zone. Another supply of air enters the kiln through a series of jets in the discharge portion of the kiln; this air is warmed by passing through the hot clinker, which is cooled thereby. The kiln

receives always the same quantities of fuel and air, with the result that for the same speed of working the temperature is constant and the burning of the materials in the kiln is regular.

The discharge orifice is provided with a triple gate to prevent loss of draught and the production of dust. The discharge is automatic and is through a double grille, both parts of which are hydraulically actuated by a push-and-pull movement. The surfaces of these grilles can be compared with that of a rough mobile grater, which breaks up the clinker, the fall and discharge of which is regular.

Kilns of this type with a diameter of about 8 ft. have given daily outputs in excess of 125 tons over a period of six months. The coal consumption is equivalent to 100,000 to 120,000 calories per 100 kg. of clinker irrespective of the nature and composition of the raw materials. Kilns of about 10 ft. diameter have produced 160 tons daily.

Bauxite in Australia.

IN a recent number of the " Journal of the Royal Society of New South Wales " an account is given by Mr. F. N. Hanlow of the distribution, composition, and origin of the bauxite and other lateritic deposits in New South Wales, which mainly occur superficially on an irregular plateau between 2,000 ft. and 3,000 ft. above sea level, and are generally ferruginous, being characterised by pisolitic nodular and earthy structures. Some high-grade deposits occur but the bulk of the material, which is found in deposits from 5 ft. to 40 ft. in thickness, has a composition within the following limits: Al_2O_3 30 to 42 per cent., Fe_2O_3 25 to 33 per cent., SiO_2 1 to 7 per cent., TiO_2 2 to 6 per cent., and ignition loss 15 to 25 per cent. The composition is essentially the same throughout the entire thickness. The ratio of alumina to ferric oxide is about 1·25, being about the same as that in the Oligocene basalts which the bauxites overlie and from which they were subsequently formed by weathering where protected from erosion. The laterisation involved removal of the alkalis and alkaline earths and almost complete desilication but practically no removal of the iron. The felspar of the basalt appears to have been converted to gibbsite. The climate was probably then tropical to sub-tropical with moderate and variable rainfall.

The Physical Properties of Hardened Portland Cement.

THE results of extensive research on the physical properties of hardened Portland cement paste have been published by Mr. T. C. Powers and Mr. T. L. Bromyard in recent numbers of the Journal of the American Concrete Institute, and the following is an abstract of the authors' conclusions. The tests related mainly to the conditions of the water in hardened paste, the properties of evaporable water, including the thermodynamics of adsorption, the density of the solids, and the porosity of the paste. It is not claimed that all the conclusions of the authors are new; on the contrary there is agreement with the belief that the colloidal state of the products of hydration is a dominant characteristic of the hardened paste. These characteristics are, however, considered in greater detail and on a quantitative basis. The relationships and data discussed in the following pertain only to specimens cured continuously at about 70 deg. F., and without modification would not apply to other conditions of curing.

Hardened Portland cement paste is not a continuous homogeneous solid, but is composed of primary particles bound together to form a porous mass. The chemical constitution of the particles is not definitely known, but it appears that many significant characteristics are dependent not primarily on the chemical constitution but rather on the physical state of the hardened paste. The extreme smallness of the particles, the smallness of the interstitial spaces, and the strong attraction of the particles for water account for the fact that changes in external conditions are always accompanied by changes in the moisture content of the hardened paste, for the changes in volume, strength, and hardness that accompany changes in moisture content, and for the relationship between ice content and temperature when the temperature of saturated or partially saturated paste is below freezing point.

Porosity

The pores in hardened Portland cement paste are considered to be the spaces that may be occupied by evaporable water, that is water which exhibits a vapour pressure greater than 6×10^{-4} mm. of mercury at 23 deg. C. It is roughly equal to the amount lost when a saturated paste is oven-dried at about 105 deg. C. The pores, exclusive of trapped air, are either capillary pores or gel pores.

Before hydration begins, and while it is plastic, a cement paste is a very weak solid held together by interparticle attraction. These forces probably act across thin films of water between the particles. The water-filled spaces between the particles constitute interconnected capillaries. When the final reactions of hardening begin the capillaries tend to become filled with solids produced by the reactions, thereby reducing the volume and size of the capillaries without destroying their continuity. Before hydration starts the volume of the capillary pores equals the volume of water. This statement is correct only for the instant when the cement and water are mixed. Solution and reaction begin at once, the average rate

during the first five minutes being higher than that during any subsequent period of five minutes. Within the initial five-minute period, the rate of reaction decreases abruptly and becomes very low, the low rate persisting under ordinary controlled laboratory conditions for about an hour. If the paste is stirred continuously during the period of rapid initial reaction, or if it is restirred at the end of that period, it remains plastic during the relatively dormant period. If it is undisturbed the paste bleeds and its volume is thereby diminished. After bleeding, the volume of the pores is equal to the volume of the remaining water-filled space (trapped air being neglected) and is approximately equal to $w_o - (V_s - cv_c)$, where w_o is the original water content after bleeding, V_s is the total volume of solid phase including the increase due to hydration and the pores in the gel, c is the weight of cement, and v_c is the volume of a unit weight of the cement. In this and subsequent equations the amount of water can be expressed in cubic centimetres or in grammes.

The volume of the solids at any stage of hydration can be estimated from $V_s = cv_c + 0{\cdot}86\ (1 + 4k)w_n$, where 0·86 is the mean specific volume of the non-evaporable water and gel water, k is a constant depending on the cement and having a value of from 0·24 to 0·28, and w_n is the weight of non-evaporable water including chemically-combined water.

Thus the volume of capillary pores is $w_e - 0{\cdot}86(1 + 4k)w_n$. During the first few hours of hydration, when w_n is small, this expression is probably not very accurate for periods during which gypsum reactions take place to an appreciable extent.

There is no capillary porosity when $0{\cdot}86(1 + 4k)w_n = w_o$ or, for an average cement for which k may equal 0·255, when $1 \cdot 74w_n = w_o$. For example, when $\frac{w_n}{c} = 0{\cdot}2$, there are no capillary pores if $\frac{w_o}{c}$ does not exceed 0·35. The highest possible water-cement ratio at which capillary pores can be eliminated by prolonged curing depends on the highest possible value of w_n and on k, both of which depend on the characteristics, including the chemical composition, of the cement. The highest value of w_n depends principally on the degree to which the cement approaches complete hydration which, in turn, depends principally on the proportion of particles finer than about 50 microns, since the coarsest particles fail to hydrate completely even though the wet-curing period is long. With an average cement, capillary pores are present even at ultimate hydration in any paste having an original water-cement ratio greater than about 0·44 by weight.

The quantity $V_s - cv_c$ is the increase in volume of the solid phase including the pores in the gel. The total porosity of the paste is the sum of the volume of the gel pores and the volume of the capillary pores. The volume of the gel pores is approximately $3{\cdot}6\ V_m$, where V_m is 25 per cent. of the weight of water that would saturate the gel, and is proportional to the superficial area of the gel. In this expression the mean specific volume of the water in the saturated gel is assumed to be 0·9. For any cement $V_m = kw_n$.

The area (sq. cm.) of the solid phase in a hardened paste is $(35{\cdot}7 \times 10^6)V_m$, and, since $k = 0{\cdot}255$ for an average cement, the superficial area of a hardened paste made from an average cement is $(9{\cdot}1 \times 10^6)w_n$. In a typical paste $\frac{w_o}{c} = 0{\cdot}6$, and the superficial area per unit volume of paste is about $2{\cdot}4 \times 10^6$ sq. cm. at ultimate hydration. Since the internal superficial area of the paste is predominately that of the gel, V_m is proportional to the superficial area of the gel.

The mean diameter of the gel pores is probably between twice and four times the hydraulic radius, m_g, which is the volume of gel pores per unit superficial area of the gel. Thus, m_g may be about 10×10^{-8} cm., and the mean diameter of the gel pores is from 20 to 40 Ångstrom units (10^{-10} metres).

The mean diameter of the capillary pores cannot be determined from data now available, but absorptivity tests indicate that the capillary pores are very much larger than the gel pores, except perhaps in pastes in which the gel nearly fills the available space.

Permeability and Absorption.

A saturated hardened paste is permeable to water. Under a given pressure gradient and at a given temperature, the rate of flow is a function of the effective hydraulic radius of the pores and the effective porosity. Indications from limited data are that the theoretical values of this function are in reasonable agreement with experimental results only for pastes containing no capillary space. It appears that cement gel has about the same permeability as granite. For pastes containing much capillary space outside the gel, actual permeability considerably exceeds the theoretical value, which appears to indicate that in such pastes the flow is predominantly in the relatively large capillary pores outside the gel. The permeability of concrete is generally greater than can be accounted for from the actual permeability of the paste, as the water is able to flow through the fissures that develop under the aggregate during the bleeding period and thus partially to by-pass the paste.

The amount of water absorbed per unit area of a dry specimen in time t during the first 30 to 60 minutes is $K_a t$, where K_a is the coefficient of absorptivity. An empirical relationship between K_a and capillary porosity was found to be

$$K_a = f[W_o - 0{\cdot}86(1 + 4k)W_n],$$

where the quantity in brackets is the capillary porosity, and where W_o is the water content of the original paste after bleeding, W_n is the non-evaporable water, and k is the constant characteristic of the cement; W_o and W_n are expressed in grammes per cubic centimetre of the specimen.

An experimental curve showed that K_a was zero, or nearly so, when there were no capillary pores. Thus the initial absorption of water by a dried specimen takes place almost exclusively in the capillary spaces outside the gel.

Properties of the Water in the Hardened Paste.

In a saturated hardened cement paste, the three classes of water recognised are non-evaporable water, gel water, and capillary water.

Non-evaporable water is a constituent of the solid material in the paste. Some of it exists as OH groups in $Ca(OH)_2$ and some, probably as water of crystallisation, in calcium sulphoaluminate. The rest is combined in the solid phase in a way not yet known, and of this part some may be combined chemically with the hydrous silicates and hydrous alumina-bearing compounds, and some may be held by physical forces. For the purpose of volume-analysis, the non-evaporable water is treated as an entity. Its volume added to that of the cement gives the absolute volume of the solid phase V_s in the paste; thus, $V_s = cv_c + w_n v_n$, where c is the cement content of the paste, w_n is the non-evaporable water content of the paste, v_c is the specific volume of the cement, and v_n is the mean specific volume of the non-evaporable water. The specific volume of the non-evaporable water is an empirical factor of about 0·82, which accounts for the observed increase in the absolute volume of the solid phase per gramme increase in the amount of non-evaporable water.

The gel water is that contained in the pores of the gel, which are so small that most if not all the gel water is within the range of the surface physical forces of the solid phase, as is indicated by the fact that the mean specific volume of the gel water is about 0·90. The vapour pressure of the gel water at a fixed temperature is a function of the degree of saturation of the gel. The lowest pressure just exceeds 6×10^{-4} m.m. at 23 deg. C., which is the highest pressure of the non-evaporable water. The highest pressure is nearly equal to that of pure water in bulk at the same temperature, the difference being due principally to the alkali hydroxides in solution. The vapour pressure at intermediate degrees of saturation will be a maximum if the existing water content was reached by continuous adsorption, beginning with a dry sample, and will be a minimum if the water content was reached by continuous desorption, starting with a saturated sample.

The weight of gel water in a saturated paste is equal to $4V_m$, where V_m is, as before, the weight required to form a complete monomolecular adsorbed layer on the solid phase. For volume analysis of the paste the weight of the gel water may be used to determine the total volume V_s (rather than the absolute volume V_s) of the solid phase in the paste. Thus, $V_s = V_s + 0{\cdot}9w_g = V_s + 3{\cdot}6V_m$, where w_g is the weight of gel water in grammes per cubic centimetre of saturated paste ($4V_m$). Like the gel water, the capillary water is a solution of alkalis and other salts, and is that which occupies space in the paste other than the space occupied by the solid phase together with pores of the gel. That is, the volume of capillary water is $V_t - V_s$ where V_t is the total volume of the saturated paste exclusive of cavities.

Practically all the capillary water lies beyond the range of the surface force of the solid phase. Hence, in a saturated paste, the capillary water is under no stress and its specific volume is the same as the ordinary specific volume of a

solution having the same composition as the capillary water. In a partially-saturated paste the capillary water is subjected to a tensile stress $\frac{RT}{Mv_f}\log\frac{p}{p_s}$ due to the curvature of the surface of the film of water and the surface tension of the water, where R is the gas constant, M the molecular weight of water, v_f the specific volume of water, p the vapour pressure of capillary water at the existing temperature and p_s saturation pressure of water at the existing temperature.

If the existing vapour pressure of the capillary water is reached by continuous adsorption from the dry state, capillary water does not exist at pressures below about $0{\cdot}45\,p_s$. Since at vapour pressures greater than $0{\cdot}45\,p_s$ and less than p_s the capillary water is present, its specific volume must be greater than unity and is a function of the tensile stress, although this has not been verified experimentally. Some of the gel water may be fundamentally the same as the capillary water. The quantity of gel water always bears a fixed ratio to the quantity of the products of hydration, whereas the quantity of capillary water is determined by the porosity of the paste.

Physical State of the Products of Hydration.

Microscopic observation of hardened paste indicates that only crystals of calcium hydroxide and the unhydrated residues of the original cement grains can readily be identified. Other microcrystalline constituents, particularly calcium sulphoaluminate, may be present in small amounts but are generally obscured by the abundant amorphous constituents. The size and volume of the pores in hardened paste indicate that the solid material is finely subdivided, although the solid particles are obviously bonded to each other. If the particles were spheres of uniform size, the diameter of each would be about 140Å. The computation leading to this size includes the volume of the microcrystalline constituents; thus the amorphous particles must be somewhat smaller than 140Å, which is in the range of colloidal sizes. Since a gel is defined as a coherent mass of colloidal material, the principal constituent of the hardened paste is the cement gel.

The cement gel is composed of products of hydration including the principal oxides, CaO, SiO_2, Al_2O_3, and Fe_2O_3, as is shown by the fact that the total superficial area of the solid phase is related to the computed composition of the cement by $\frac{V_m}{w_n} = 0{\cdot}230(C_3S) + 0{\cdot}320(C_2S) + 0{\cdot}317(C_3A) + 0{\cdot}368(C_4AF)$, where the symbols in parentheses represent the computed weight-fraction of the compounds indicated. The similarity of the numerical coefficients and sizes of the particles given in the foregoing show that all constituents may be present in a single complex hydrate of high specific surface or they may be constituents of two or more different hydrates having similar specific surfaces. The relative smallness of the coefficient of C_3S agrees with the fact that this compound hydrolyses to give microcrystalline (low specific surface) $Ca(OH)_2$ as one of its products of reaction.

Changes of Energy.

The total amount of heat evolved upon hydration is directly proportional to the total amount of non-evaporable water in the paste, the proportionality constant varying with the composition of the cement. For Portland cement, the heat evolved is from 485 to 550 calories per gramme of non-evaporable water. The total heat of hydration is the sum of the heat of combination of the non-evaporable water, the net heat of adsorption of water on the surface of the solid phase, and the net heat of capillary condensation. The net heat of superficial adsorption is the amount of heat in excess of the normal heat of liquefaction that is evolved when water vapour interacts with the solid phase, and for all cement pastes is approximately $472V_m$ calories when the paste is changed from the dry to the saturated state.

Adsorption at low vapour pressures causes the solid phase to become covered with a film of water having a superficial area presumably equal to the area of the solid phase covered. At pressures above $0{\cdot}45p_s$ adsorption is accompanied by capillary condensation which progressively diminishes the exposed water surface as the pressure is raised. The heat evolved from the destruction of the water surface is the net heat of capillary condensation, which is approximately $100V_m$ calories when a paste is changed from the dry to the saturated state.

The total net heat of adsorption is the sum of the total net heat of surface adsorption and the total net heat of capillary condensation, that is approximately $572V_m$ calories, which is about 670 ergs per square centimetre of solid surface and is about the same as the heat of immersion of various mineral oxides in water. It is also practically equal to the decrease in enthalpy of the system, which is the sum of the decreases of free energy and unavailable energy; the decrease in unavailable energy is the product of the decrease in entropy and the absolute temperature.

Shrinking and swelling, moisture diffusion, capillary flow, and all other effects involving changes in moisture content of the paste at constant temperature are due to the free surface energy of the solid phase, or to the free surface energy of the water, or to both. All such effects are accompanied by a decrease in free energy and, in this case, a decrease in entropy, but the forces producing these effects are derived solely from the free energy. The decrease in free energy is a function of the ratio of the vapour pressure of the adsorbed water to that of free water at the same temperature without regard to the nature of the underlying solid phase, and equals $75{\cdot}6\ log\frac{p}{p_s}$ calories per gramme of water. It thus varies from nothing when $p = p_s$ to a very large value when p is very much smaller than p_s.

A change in entropy denotes an internal change in the substances involved in a reaction. In this case the change is assumed to take place solely in the water as it changes from the free to the adsorbed state. The estimated decrease in

entropy ranged from 0·22 calories at $p = 0{\cdot}5p_s$ to 0·50 calories per gramme per degree C. at $p = 0{\cdot}05p_s$. The magnitude of the decrease in entropy indicates that some of the water is changed by adsorption in this range of pressures more than free water is changed by freezing under ordinary conditions, and as much as or more than free water is changed by becoming water of crystallisation. Water adsorbed at $p = 0{\cdot}05p_s$ undergoes a change as great as the change from ordinary water to the hydroxyl groups chemically combined in $Ca(OH)_2$.

The decrease in enthalpy is a measure of the energy that must be supplied to restore adsorbed water to the normal liquid state. The maximum energy of binding of the adsorbed water is estimated at about 400 calories per gramme of water, the average for the first complete adsorbed layer being about 300 calories. The average energy of binding of the gel water is about 143 calories per gramme of gel water. These figures, which are probably too low as the effect of absorbed air was neglected, indicate that most of the non-evaporable water is less firmly bound than the water in $Ca(OH)_2$ for which the energy of binding is 847 calories. The capillary water cannot be considered bound in the same sense as the non-evaporable water and gel water. The energy required to remove all the capillary water from a saturated paste, if that could be done separately, would be $100V_m$ calories, regardless of the amount of capillary water in the paste.

Change of Volume.

Cement paste shrinks or swells as the cement gel loses or gains water. Swelling results when the surface forces of the solid phase are able to draw water into the narrow spaces between the solid surfaces. The amount of the swelling can be accounted for by assuming that the total change of volume that occurs when a dry specimen is saturated is due to the increase in spacing of the solid surfaces required to accommodate a monomolecular layer on each opposing solid surface. The shrinking which occurs when water is withdrawn from the gel is probably due to the solid-to-solid attraction that tends to draw the solid surfaces together, although capillary tension and elastic behaviour may also be involved. By this theory change of volume is regarded as the result of a lack of balance in the forces of solid-to-liquid attraction and capillary tension acting on the adsorbed water. When the forces are equal the volume of the gel remains constant.

Swelling pressure is the force that would be just able to prevent water from entering the gel. For isothermal swelling, the increase over the existing external pressure required to prevent swelling equals the increase in free energy of the adsorbed water when swelling occurs divided by the specific volume of adsorbed water (assumed to be independent of pressure). Expressed in terms of the change in vapour pressure of the adsorbed water that accompanies swelling, the swelling pressure is $-\frac{RT}{Mv_f} log \frac{p}{p_s}$; this expression is probably reasonably accurate except for low values of $\frac{p}{p_s}$ for a hypothetical gel composed of discrete

colloidal particles, but when the gel is composed of interconnected particles and encloses stable microcrystals and aggregate particles, as in concrete, shrinking or swelling is partially opposed by elastic forces. Hence some difference between the theoretical and actual swelling pressure should be expected.

In a partially-saturated paste the tendency of the water to enter the gel is opposed by tension in the capillary water. The force of capillary tension is $\sigma\left[\frac{1}{r_1}+\frac{1}{r_2}\right] = -\frac{RT}{Mv_f}\log\frac{p}{p_s}$, where σ is the surface tension of water and r_1 and r_2 are the principal radii of curvature of the menisci. Thus capillary tension and potential swelling pressure have the same relationship to relative vapour pressure except for a small difference in v_f; when the vapour pressures of the gel water and the capillary water are equal, the volume remains constant.

When drying occurs, capillary water and gel water are lost simultaneously. Since the resulting change in volume is due only to the change in the amount of gel water it can be shown that the change in volume per unit change in total water content depends on the ratio of capillary water to total water.

When cement and water react there is a reduction in the sum of their absolute volumes. On the assumption that the contraction is confined entirely to the water and that the total apparent volume of the hardened paste does not change after bleeding has finished, the weight of total water in the saturated hardened paste w_t multiplied by the mean specific volume of the total water v_t equals the volume of the original water in the paste w_o. The difference between w_o and w_t is the amount of water that must be absorbed during hydration for the specimen to remain saturated. At any stage of hydration $v_t = 1 - 0{\cdot}279\frac{w_n}{w_t}$. Hence the contraction of the water in cubic centimetres is $0{\cdot}279w_n$.

If a specimen is kept sealed after the bleeding period, so that no extra water is available during the course of hydration, the pores in the paste become partially emptied. This is called self-desiccation, which is believed to be an important factor in the resistance of concrete to frost. Experimental evidence indicates that when specimens of good quality are stored in moist air, or even under water, they are unable to absorb enough water to compensate completely for self-desiccation. Consequently, cement paste is seldom found in a completely saturated state, and hence is seldom in a condition immediately vulnerable to the action of frost. The ratio of empty-pore volume to total-pore volume (ignoring differences in specific volume) can be shown to be $\frac{0{\cdot}279w_n}{w_o - 0{\cdot}721w_n}$, which gives the deficiency in evaporable water on a weight-ratio basis, which is close enough to the volume ratio for practical purposes.

Capillary Flow and Moisture Diffusion.

Capillary flow and moisture diffusion are considered thermodynamically to be the result of inequalities in free energy, which under isothermal conditions arise from inequalities in moisture content, in deformations of the solid phase, and in

the external pressure acting on the adsorbed water. When such inequalities arise the evaporable water always tends to redistribute itself in such a way as to equalise its free energy. This has an important influence on plastic flow under sustained stress.

Effect of Temperature Changes at Constant Moisture Content.

As already mentioned, potential swelling pressure and capillary tension are related. At constant water content a rise in temperature expands the capillary water and thus decreases its surface curvature, and decreases the surface tension, and consequently decreases capillary tension and thus causes water to enter the gel, which in turn causes swelling in addition to ordinary thermal expansion. The swelling of the solid phase does not occur in a dry specimen or in a saturated specimen where $p = p_s$. It follows therefore that the thermal coefficient of concrete is not constant unless the concrete is completely dry or saturated. When counteracting effects are absent, evaporable water moves in the direction of descending temperature.

In concrete subjected to changing external forces, changing temperatures, and fluctuating ambient humidity, the evaporable water must be in a continual state of flux. Consequently the concrete swells, shrinks, expands and contracts under the changing conditions in a highly complicated way. The separate effects may combine in different ways at any point in the mass so that they offset or augment each other. Possibly these effects have an influence on the ability of concrete to withstand weathering.

The Extent and Rate of Hydration of Portland Cement.

The principal factors governing the ultimate degree of hydration, regardless of the time required, are the relative proportion of particles having mean diameters greater than about 50 microns, and the original water-cement ratio. Incomplete data indicate that a cement containing no particles larger than 50-microns becomes completely hydrated if the water-cement ratio is not too low. The ultimate extent of hydration appears to be approximately inversely proportional to the residue on a 325-mesh sieve. The ultimate degree of hydration is proportional to the water content of the paste if the water-cement ratio is less than a definite limiting value, which for an average Portland cement is about 0·44 by weight. Presumably the greater the sieve residue on a 325-mesh, the lower the limiting ratio.

With other factors equal, the average rate of hydration is lower the smaller the water-cement ratio except during a short initial period. Consequently the time required to reach ultimate hydration becomes longer as the ratio decreases. During the first week or two the rate of hydration is higher by a large amount the higher the specific surface, but during the later stages the rates of hydration for cements of widely different specific surfaces differ comparatively little.

Self-desiccation influences the rate of hydration. As the pores become partly emptied the vapour pressure of the remaining evaporable water is correspondingly

reduced. Experiments indicate that, even though the remaining water is chemically free, its rate of reaction with cement is a function of its relative vapour pressure, which if below about 0·85 results in hydration virtually ceasing. Consequently sealed specimens hydrate more slowly than those having access to water, and they may never reach the ultimate degree of hydration possible when extra water is available. This has a bearing on the efficiency of membrane curing.

The foregoing indicates that conclusions concerning the rate and amount of hydration of Portland cement in concrete having a water-cement ratio between 0·45 and 0·70 should not be drawn from data on test pieces which may have a ratio of 0·25. Moreover, specimens cured in sealed vials should not be expected to hydrate at the same rate and to the same extent as similar specimens cured in water or fog. Also it should be noted that, for samples in sealed vials, water separated from the paste by bleeding must be considered as extra water.

Relation of Paste Porosity to Compressive Strength.

The compressive strength of 2-in. mortar cubes is, with certain restrictions, given by $120{,}000 \frac{V_m}{w_o} - 3{,}600$ lb. per square inch. The ratio $\frac{V_m}{w_o}$ is proportional to the degree to which the gel fills the originally water-filled space, that is the gel-space ratio. The relationship holds for all ages and apparently for all cements low in C_3A (less than about 7 per cent. computed). For a cement of average or high C_3A content, and especially for those high in both alkali and C_3A, the strengths obtained are lower than those indicated by the equation, but can be brought into compliance therewith by increasing the amount of gypsum in the cement. The equation is empirical and the variables not adequately considered include some features of the composition of the cement, the effect of aggregate particles, trapped air, fissures that form under the aggregate particles during the bleeding period, and variations in curing temperature.

Freezing of Water in Hardened Paste.

Owing to the relationship between water content and free energy, as shown by sorption isotherms, the water in a saturated paste freezes or melts progressively as the temperature is varied below the ordinary melting point. The capillary water is believed to freeze in place, but the gel-water probably flows or distills from the gel to the capillaries before it freezes. The final melting point, which is the temperature at which the last increment of ice disappears on progressive melting and which would be the same as the initial freezing point were it not for the occurrence of supercooling, is from about — 1·6 deg. C. to about — 0·05 deg. C. for saturated pastes. The lowering of the final melting point is due to dissolved material in the mixing water, principally alkalis. The final melting point in a paste that is not fully saturated depends not only on the dissolved material but also on the degree of saturation, the lower the degree of saturation the lower being the final melting point.

All the evaporable water is freezable, but a minimum temperature of about — 78 deg. C. is required to freeze it all.

At any given temperature between — 78 and — 12 deg. C., the maximum amount of freezable water in saturated paste is $w_o - (0.721 + 0.26u)w_n$, in which w_e is the total evaporable water, V_m is a factor here considered to be proportional to the gel content of the paste, w_n is the non-evaporable water, and u is a constant equal to the amount of water unfreezable at a given temperature divided by V_m.

The following are empirical relationships for the maximum amounts of water freezable in saturated pastes at given temperatures, in terms of w_n and w_o: at — 12 deg. C., $w_o - 1.76w_n$; at — 20 deg. C., $w_o - 1.68w_n$; at — 30 deg. C., $w_o - 1.55w_n$. At — 12 deg. C. the amount of freezable water is equal to the volume of the capillary water outside the gel. At lower temperatures gel-water is frozen, but the gel-water probably leaves the gel and becomes part of the ice already formed in the capillaries. At temperatures above — 12 deg. C. the maximum amount of freezable water is roughly proportional to the amount of capillary water, $w_e - 4V_m$.

The maximum amount of ice will not be present unless the temperature has previously dropped to a low value, say — 50 deg. C. or perhaps lower. If the maximum cooling is only a few degrees below the final melting point, the amount of ice formed would probably be less than the amount indicated by the relationship given. For practical purposes, the freezable water can be considered to be identical with the capillary water. Hence, pastes that contain no capillary space outside the gel are considered to be without freezable water.

High-Alumina Cement in Japan.

ALTHOUGH Japan is short of minerals that are naturally rich in alumina, such as bauxite, the discovery of strata of aluminous materials lead the Osaka Yogyo Cement Co. to manufacture a special cement the chemical composition of which is: SiO_2, 6 per cent. to 8 per cent.; Fe_2O_3, 1 per cent. to 3 per cent.; CaO, 36 per cent. to 38 per cent.; and Al_2O_3, 50 per cent. to 55 per cent. The specific gravity is from 2·93 to 2·98. According to a description of this cement in a recent number of "Revue des Materiaux de Construction," the setting times are a little short because of the low amount of Fe_2O_3 and the high proportion of alumina.

Tests on plastic mortar specimens and specimens of relatively dry mortar have demonstrated that the cement paste has not a high strength at early ages. From a study of the resistances obtained at curing temperatures of 20 deg., 50 deg., and 75 deg. C., it is shown that high temperatures are injurious to this cement in the same way as they are to the high-alumina cements produced in other countries. The usual degree of fineness represented as a residue on a sieve of 4,900 meshes per square cm., between 3·5 per cent. and 10 per cent., is necessary as extremes of fineness or coarseness do not give a high-alumina cement of superior quality.

The Cement Industry Abroad.

IN our number for March 1947, we gave some particulars of the cement industry in certain foreign countries. In the following similar information relating to other countries is given.

Mexico.

The improved position of the Portland cement industry in Mexico is described by Sr. F. Barona in "Cemento-Hormigon" for December, 1946. In 1942 there were eight cement works having a total annual capacity of about half a million tons. In 1946 the annual capacity was about doubled, and by the end of 1947 it is expected that the number of works in operation will be seventeen and the total capacity will increase to about 1¾ million tons annually. About two-thirds of this potential quantity will be produced by eight works in the central zone of the country.

The daily productive capacity would be about 6,000 tons and a multiple of 300 was used in ascertaining the annual capacity; this multiple represented the number of days, in one year on which a factory was assumed to be working normally and allowed for time spent on repairs, replacements, breakdowns, and delays in delivery of fuel and raw materials.

Sweden.

The consumption of cement in Sweden during 1946 reached a new high record owing to the continued increase in building and the increasing shortage of other building materials. According to the annual report of Skanska Cement AB, the consumption in 1946 exceeded the high figure for 1945 by 21 per cent. and was 50 per cent. higher than in 1939. The quantity of cement produced by the company during 1946 was 864,500 tons, and the capacity of the works has been used to the full.

Poland.

In 1939 there were eleven cement works in Poland with a capacity of 1,810,000 tons. Production in 1938 was 1,720,000 tons. Two of these works are in the territory ceded by Poland to the U.S.S.R. The remaining nine works were little damaged during the war and represent 94 per cent. of the pre-war capacity

There are several cement works in the former German territory now occupied by Poland, but these have been severely damaged. They comprise seven works with pre-war annual capacities of between 300,000 tons and 35,000 tons (total capacity 1,035,000 tons) and five smaller works. During the war the enforcement of maximum production without necessary repairs led to a considerable wearing-out of machines and to the diminishing of capacity by more than 60 per cent. Only four works, although entirely dismantled, were taken over in a condition which enabled them to be operated after some repairs. These are the works in Groszowice, Opole City, Nowa Wieś, and Podgrodzie with a total pre-war capacity of 635,000 tons.

The Polish cement industry produced in 1946 only 1,300,000 tons compared with the pre-war production of 1,719,000 tons. Reconstruction of this industry is expected to increase the production to 1,450,000 tons in 1947, 1,700,000 tons in 1948 and 2,000,000 tons in 1949. About 9,000 workers are now employed in the industry. It is expected that 1,500,000 tons will be exported in these three years. Of the total production of 54,365 tons in February, 1947, 22,330 tons were exported.

Production of Lime in Poland.

The amount of lime produced in Poland in 1946 was 360,000 tons, compared with 51,000 tons in 1945. The production in 1947 is expected to reach 500,000 tons.

Polish Standard Specifications for Ordinary Portland Cement.

REVISED standard specifications for ordinary Portland cement were published in Poland in 1946 and consist of five documents giving respectively (i) the requirements for ordinary Portland cement ; (ii) Vicat test for setting-time and other physical tests ; (iii) procedure of the tests for chemical composition ; (iv) procedure and apparatus for the mechanical tests ; and (v) clauses relating to the delivery and sampling of Portland cement. The dates of the previous issues of these standards which the present documents supersede are (i) 1939, (ii) and (iii) 1926, (iv) 1931, and (v) 1928.

The requirements for fineness are that not more than 3 per cent. shall be retained on a sieve having an aperture of 0·2 mm., and not more than 25 per cent. on a sieve having an aperture of 0·08 mm. Initial setting time shall be not less than 40 minutes and the final setting not more than 10 hours. The chemical composition shall comply with the following : SO_3, not more than 2·5 per cent. ; MgO, not more than 5 per cent. ; insoluble residue, not more than 1·5 per cent. ; loss on ignition 5 per cent.

The resistance to tension is measured by means of a beam test similar to the test for the modulus of rupture of concrete. The test piece is 160 mm. long, 40 mm. wide, and 40 mm. deep, and is composed of a mixture of one part of Portland cement to one part of fine sand to one part of coarse sand to 0·6 part of water ; one part is 450 gm. The test piece is supported on two rounded supports placed 100 mm. apart and 10 mm. from each end of the test piece. The load is applied at the centre of the test piece. The minimum tensile strength required at 7 days is 427 lb. per square inch and at 28 days 711 lb. per square inch. Compression tests on cubes made of the same mixture must show a strength of not less than 1,849 lb. per square inch at 7 days and 3,536 lb. per square inch at 28 days.